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6. AUTHOR(S)
Felix E. Fernández

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Puerto Rico
Mayaguez Campus
Department of Physics
Mayaguez, PR 00680

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13. ABSTRACT *(Maximum 200 words)*
Pulsed Laser Deposition (PLD) was used in order to fabricate thin films of various classes of materials of interest for future nonlinear optical waveguide devices. Materials investigated included potassium niobate, potassium tantalate niobate (KTN), and aluminum nitride. SiO_x films were also grown and studied as a step in producing doped-glass films via PLD. The films were characterized with several techniques, including Rutherford Backscattering Spectroscopy, X-ray diffraction, optical microscopy, electron microscopy, and when feasible, ellipsometry, and UV-visible light transmission. In addition, a method was devised to enhance the thickness uniformity of PLD-fabricated thin films, which is notoriously poor. This method uses a conic optic of novel design in order to produce concentric annular sources at the target being ablated. In principle, uniform coverage within few percent is achievable for substrate sizes of a few inches, using current technology.

14. SUBJECT TERMS
Thin films, pulsed laser deposition, KTN potassium niobate, potassium tantalate, aluminum nitride, thickness uniformity

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Pulsed Laser Deposition of Thin Film Materials for Nonlinear Waveguides

Félix E. Fernández

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Grant Number DAAL03-90-C-0213

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University of Puerto Rico
Mayagüez Campus

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Foreword

This project has emphasized the development, via pulsed laser deposition (PLD), of thin film materials of interest in terms of optical nonlinearities. Direct testing of nonlinearities by using the films as waveguides, as originally planned, was impeded by the thickness nonuniformity of the films obtained by PLD. Accordingly, part of the research effort was dedicated to overcoming this obstacle. Efforts in this direction were eventually successful, although implementation of the method devised is still in progress. In parallel with this, the materials research effort was augmented to include classes of materials not directly considered in the original project, but with considerable promise for future NLO device application. In retrospection, this was probably overly ambitious for a single researcher, particularly against the backdrop of the deficient infrastructure for research. On the other hand, the effort has created an ample foundation which ensures continuity and has facilitated initiation of collaborative efforts.

The equipment acquired through this grant provided a substantial basis for conducting and continuing research in this area. Main facilities established include a PLD system with capability for UHV operation, automatic sequential deposition, substrate heating up to 1000°C in oxygen atmosphere, residual gas analysis, and thickness monitoring with a quartz microbalance. Additional equipment, in some cases obtained with partial support from other sources, include a multispectral ellipsometer, an updated XRD diffractometer and powder diffraction database, wide angle Debye-Scherrer camera. An analysis chamber was also designed and built to work with the original PLD chamber without breaking vacuum. It is currently being equipped with capability for LEED, Auger, and ellipsometric studies of samples. In order to enable ion-assisted PLD growth of materials, particularly nitrides, a Kaufman type ion gun was recently ordered, and required system modifications are being performed. Detection and precision positioning equipment was also acquired for optical measurements. A Raman shifter, to provide a tunable light source pumped by an existing dye laser, was designed and built in-house, and is currently operational. Additional funding from other sources has been obtained for continuing work.

The work conducted through this project has generated much interest and has stimulated a number of collaborative efforts. In the Department of Physics at UPR-Mayagüez, it has attracted more graduate students than any other existing project. In fact, the number of graduate students working on some aspect of it is limited mainly by this researcher's available time to responsibly direct their work. Two students working directly on this project completed their M.S. degrees, and two more will complete this semester. Two other students are continuing related work at present. Collaboration with two new faculty members, Professors Huimin Liu and Weiji Jia, with ample experience in experimental nonlinear optics and spectroscopy has been initiated. Collaboration with Professor Ram Katiyar, of UPR-Rio Piedras, was also recently started. Professor Katiyar has ample experience and resources for doing Raman Spectroscopy studies of the films.

In summary, while not all the initial objectives of this project have been accomplished at the present time to this researcher's satisfaction, the stimulus provided to him, his students, and to research associates has been considerable. At the end of this period of performance, this researcher views this effort certainly not as a finished project, but as the start of a long-range and stimulating endeavor. For this he is grateful to the U.S. Army Research Office.

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Problem Statement

Pulsed Laser Deposition (PLD) has been growing in importance in recent years as a thin film growth technique particularly suitable for classes of materials including complex oxides and wide bandgap semiconductors. Some of these hold considerable promise for application in nonlinear optical waveguide devices. The main thrust of this project has been the development of these thin film materials by PLD, and their physical and optical characterization.

The potassium niobate-tantalate (KTN) crystal family is a transparent ferroelectric with remarkable nonlinear optical properties. In addition, the properties, including the Curie temperature, can be tailored within a range by controlling the Nb:Ta ratio in the material. However, KTN is a quaternary material which is hard to grow with sufficient quality by standard methods. PLD growth of this and similar materials offers an attractive route, compatible with much of the existing PVD technology. The possible advantage of PLD in this case is mainly through the easier control of stoichiometry provided, if composite targets are used.

Thin film growth of nitride wide bandgap semiconductors is also viable by PLD. From the point of view of integrated optic applications, the direct-transition semiconductors AlN and GaN are of particular interest. These materials form a solid solution for which the bandgap can be tailored from 3.2 to 6 eV. Their crystalline structure is the same, with very similar lattice parameters. Another advantage is the very high thermal conductivities exhibited, which make them attractive as waveguide materials. The possibilities $Al_{1-x}Ga_xN$ films and multilayers for nonlinear optical devices operating in the UV remains to be explored. In comparison with many other PVD techniques, PLD presents the advantage of better resulting stoichiometry for growth of these nitrides. In addition, the high kinetic energies of evaporant species can facilitate crystal formation without the need for elevated substrate temperatures.

Doped-glass materials present very attractive possibilities for nonlinear waveguide devices. In particular, semiconductor-doped and noble-metal-doped glasses have shown some of the highest third order nonlinear optical coefficients for inorganic materials. The possibilitily of employing PLD to fabricate these was deemed

promising due to the possibility of incorporating materials in very small quantities during deposition. Still, microcrystals would likely have to form through the usual "ripening" process, leading to an undesirably wide range of sizes. More recently, interest has augmented due to reports of production of very uniform microdroplets through laser ablation.

This research project was conducted as an exploration of the possibilities of PLD for growth of the thin film materials mentioned above. In particular, the feasibility of fabricating waveguides out of them was kept as a central issue. This emphasis forced special attention on two features of PLD: the nonuniformity of resulting film thickness distribution, and the occurrence of high particulate concentrations in the deposited materials.

Results Summary

KTN Materials

Growth of KTN, $KNbO_3$, and $KTaO_3$ films was attempted by PLD from, respectively $KTa_{0.33}Nb_{0.67}O_3$, $KNbO_3$, and $KTaO_3$ targets. The two latter materials were grown in preparation for multilayer fabrication of KTN, a more flexible approach than growth direct from KTN targets. However, as many of the physical properties of these materials are very similar it may be supposed that many results are interchangeable. A wide range of conditions were explored, including: substrate temperatures from ambient to over 700°C, background pressures from high vacuum to 2 Torr O_2, laser fluence from 1 to $>$ 10 J/cm^2, both 355 and 532 laser wavelength, and a variety of substrate materials. Deposits were studied with RBS, XRD, and optical microscopy techniques.

In general, for all conditions encompassed in the study, the deposits were extremely rough, the result apparently of accretion in micron-sized globules. Only for growth conducted in O_2 pressures of a few hundred mTorr did a uniform film appear. This was, however, accompanied by the same globular formations observed for samples grown at lower pressures. In terms of stoichiometry, the films were always potassium deficient. Typically, only 80 % of the required potassium remained in the film. Substrate temperature has a major influence in the film microstructure. Only for temperatures near 700°C or higher were the desired perovskite phases observed exclusively, as shown in the XRD scan in Figure 1 (all Figures in Appendix I). At lower temperatures other phases, including simpler constituent oxides are formed. A larger amount of amorphous material is also formed at lower temperatures and higher beam fluences. Annealing in air after deposition promotes crystallization of the amorphous material, but, unfortunately, not just into the perovskite phase. Samples grown at lower fluences (few J/cm^2) and high substrate temperatures are mostly polycrystalline, with observable phases corresponding only to the target material composition, in spite of the marked potassium deficiency. Surprisingly, films grown with 532 nm light pulses showed almost exclusively perovskite phase composition, while films grown with 355 nm light evidenced a mix of the perovskite and pyrochlore phases. At

present no satisfactory explanation is offered for this fact. Films grown on glass substrates had completely random crystallite orientation (Figure 1a). No significant orientation effect was observed for growth on (100) Si or (0001) sapphire (Figure 1b) substrates. On the other hand, clear orientation was exhibited for growth over (100) oriented MgO substrates. For $KNbO_3$, growth was mainly along the (110) direction in this case (Figure 1c). For KTN and $KNbO_3$, detailed XRD examination of the peaks corresponding to the perovskite phases observed were found to split into those conforming to the orthorhombic phase, as could be expected (Figure 2).

The large number of particulates and globular accretions observed in the films is the main difficulty encountered. There appears to be some relationship between this and the quality of the target used. All targets used, which were commercially obtained, had densities substantially lower than that of the bulk material. For PLD this can have a considerable influence in the resulting films. In the near future we will be fabricating targets by means of the sol-gel technique. It is expected that denser targets will result, which should lead to improved films. In order to attain better control of the stoichiometry, deposition directly from the component oxides will be studied as well. As shown recently by other workers, the observed potassium deficiency in the films can be overcome by enriching the film through a simultaneous or sequential deposition from a suitable potassium compound. Our initial efforts in this direction, using a potassium carbonate target, were not successful at the fluence regimes employed. More detailed work is required in this connection, but it will be carried out when better targets are available.

Aluminum nitride

AlN films were produced by PLD from AlN targets, in a nitrogen atmosphere, and in vacuum. As for the case of the KTN materials, an ample range of growth conditions were explored. Best results were obtained at substrate temperatures of near 650_0C, in high vacuum, or with nitrogen pressures of up to 20 mTorr, and fluences of approximately 1 J/cm^2. This is not much higher than the ablation threshold for this material. High fluences tend to produce a high aluminum content

in the film. Laser beam wavelength also had a marked effect, with UV light (355 nm) producing better quality films, with very few particulates, micron or sub-micron sized. Except for these inclusions, films grown under these conditions are transparent and optically smooth, showing clear interference bands and no observable features under the optical microscope. Stoichiometrically, the films are nitrogen-deficient, as has been observed by others. Apparently associated with oxygen content, the films have a broad absorption peak at 250 nm. Growth of AlN met with the complication of oxygen incorporation, as confirmed with RBS measurements. We improved matters by laser-etching the target prior to deposition, and by installing an oxygen trap in the N_2 line. A high oxygen concentration is still present in the films. In Figure 3 an RBS spectrum of one of the samples is shown. For this case the atomic percent contents of Al, N, and O are, respectively 46.8, 37.6, and 15.6, respectively. Most of the oxygen appears to be near the substrate, however. Based on these RBS results, ellipsometric measurements, and subsequent modelling, we are now inclined to believe that most of the oxygen is near the substrate and may be caused by contamination of the target surface itself. This cannot be effectively removed by the laser etch step unless the vacuum is mantained prior to deposition.

Microstructurally, the films are polycrystalline, evidencing the hexagonal AlN structure almost exclusively. Growth tends to occur with some preferred orientation of the c-axis perpendicular to the substrate plane, even on amorphous substrates. Oriented growth was obtained on (1102) sapphire substrates, in which case a single, well developed AlN peak corresponding to (0002) planes was observed in XRD scans, as shown in Figure 4.

Some tests were performed growing films from aluminum targets in nitrogen atmosphere instead of from AlN targets. These films are essentially aluminum. On the other hand, AlN films can be grown from AlN targets even in vacuum. Since the nitrogen molecule has such a high binding energy, it can be concluded that the important factor in formation of AlN is the availability of nitrogen atoms or ions. AlN targets can easily be or become Al-rich. It is necessary to provide an assist during growth in the form of nitrogen ions. Some very recent research by other workers,

particularly for GaN, supports this idea. We are currently completing some modifications of our PLD system, including the addition of a high flux nitrogen ion gun, with the main purpose of producing stoichiometric AlN and similar films and multilayers. This work will be expanded in the near future to growth of InN and GaN, and multilayered structures of these. Doping and metallization of these materials are very attractive problems, which will be addressed in collaborative efforts.

Silica films

It is not possible to grow silica films with reasonable quality by PLD directly from SiO_2 targets, at least for the laser wavelengths available to us (532 nm, 355 nm). Instead, we grew glass films by PLD from Si targets in an oxygen atmosphere. Best results in terms of surface quality were obtained with 355 nm light pulses, fluences of order 1 J/cm^2, and oxygen pressures of few mTorr. In terms of stoichiometry, the films were $SiO_{1.85}$. Structurally they were amorphous, as expected. Ellipsometric measurements of the optical properties in the visible range gave results generally close to published data for amorphous SiO_2. Ultra-thin gold films were also deposited, with very satisfactory results. This work is the basis for continuing work with noble-metal doping of silica glass films.

Film thickness uniformity

Initially, it was attempted to alleviate this problem by means of cylindrical optics and target geometries. While there was some improvement, this proved inadequate. Later, taking a different approach, a novel uniformity-enhancing scheme for thin films grown by PLD was devised. The details are presented in a manuscript, which was recently submitted to Journal of Vacuum Science and Technology A. A copy was duly submitted to ARO and the details will not be repeated here. This work generated a patent application, already reported to ARO.

Lack of beam uniformity is one of the key issues affecting generalized applicability of PLD. In particular, due to the tight thickness control required for planar waveguides, the possibility of fabricating structures with useful areas of any

reasonable size depends on this issue to a greater degree than for most applications. While approaches such as beam scanning or substrate motion have been used before to enhance film thickness uniformity, to my knowledge these have not been systematized. The analysis I have completed can be useful in providing rules for fabrication of large-area films or multilayers by PLD with beam scanning. I expect to implement this approach in the near future. The method presented in the manuscript, however, is more general. It emphasizes annular light distributions at the target instead of scanning the beam into a circle. In addition, I introduce the means to generate annular light distributions onto the target for radially symmetric laser beams. There will be technical difficulties in applying this method. In particular, any deviation from the radial symmetry in the beam will degrade the resulting thickness uniformity of the film. Also, applicability is limited by available laser power. Taking into consideration the equipment available to me at this time, I have opted for the scanning method. An advantage of this is that it can be used also with lasers which do not have circularly symmetric output, such as excimer lasers. Due to instrumental difficulties it will not be possible to implement this until later this year.

Publications, and Technical Presentations

Publications:

Enhancement of Thickness Uniformity of Thin Films Grown by Pulsed Laser Deposition
F.E. Fernández
Submitted to Journal of Vacuum Science and Technology A.

Technical presentations:

Thin Films by Pulsed Laser Deposition
F.E. Fernández
Arizona Research Laboratories, Surface Science Division
University of Arizona, October 13, 1992.

Pulsed Laser Deposition of Thin Film Materials
(Poster presentation)
F.E. Fernández and P. Marrero
Eighth Annual EPSCoR Conference,
Las Vegas, Nevada, Oct. 14-16, 1992.

Potassium Tantalate-Niobate Materials Grown by Pulsed Laser Deposition
F.E. Fernández and C. Hernández Sherrington
Joint AAAS - EPSCoR Annual Conference 1993
Mayaguez, P.R., Feb. 6, 1993.

Pulsed Laser Deposition of Potassium-Niobate-Tantalate Thin Films
(Poster presentation)
F.E. Fernández and C.A. Hernández
P.R. Materials Research Center Mini-Gordon Conference
Lajas, P.R., Dec. 1993.

Aluminum Nitride Thin Films by Pulsed Laser Deposition
(Poster presentation)
F.E. Fernández and G.F. Restrepo
P.R. Materials Research Center Mini-Gordon Conference
Lajas, P.R., Dec. 1993.

Growth and Characterization of Thin Films by Pulsed Laser Deposition
F.E. Fernández, G.F. Restrepo, C.A. Hernández, and J. Aparicio
Sixth P.R. EPSCoR Annual Conference, San Juan, P.R.
May 6-7, 1994.

Participating Scientific Personnel

Félix E. Fernández - P.I.	
Nelvin Rodríguez	Graduate Student
Loren I. Espada	Graduate Student - Completed M.S. in October 1993.
Gerson F. Restrepo	Graduate Student - Completed M.S. in July 1994.
Cecilia Hernández	Graduate Student - Expected to complete M.S. in November 1994.

Additional students participating aspects of this project but supported through other funds:

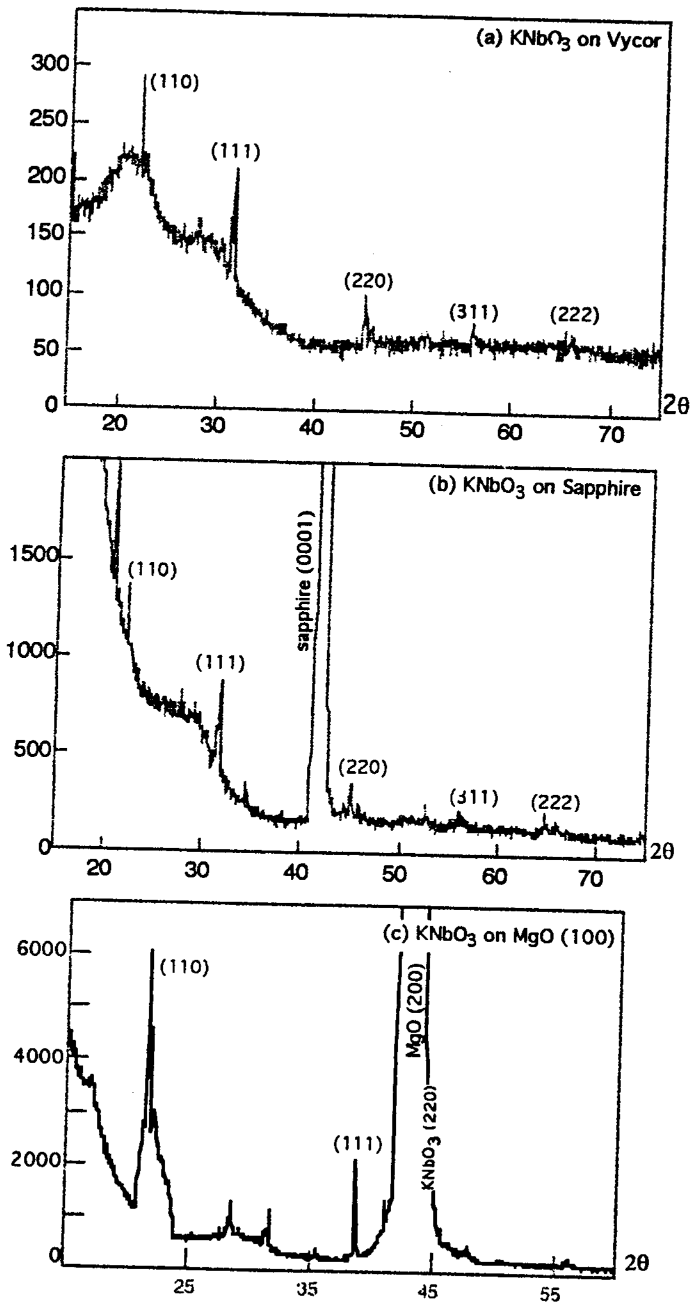
Andrés Enríquez	Graduate Student - Expected to complete M.S. in December 1994.
Joaquín Aparicio	Graduate Student - Expected to complete M.S. in December 1994.
Pablo Marrero	Graduate Student - Expected to complete M.S. in May 1995.

Report of Inventions (by Title Only)

Method of Depositing Target Material on a Substrate and Lens for doing Same.
Patent Application Serial No. 08/027,191

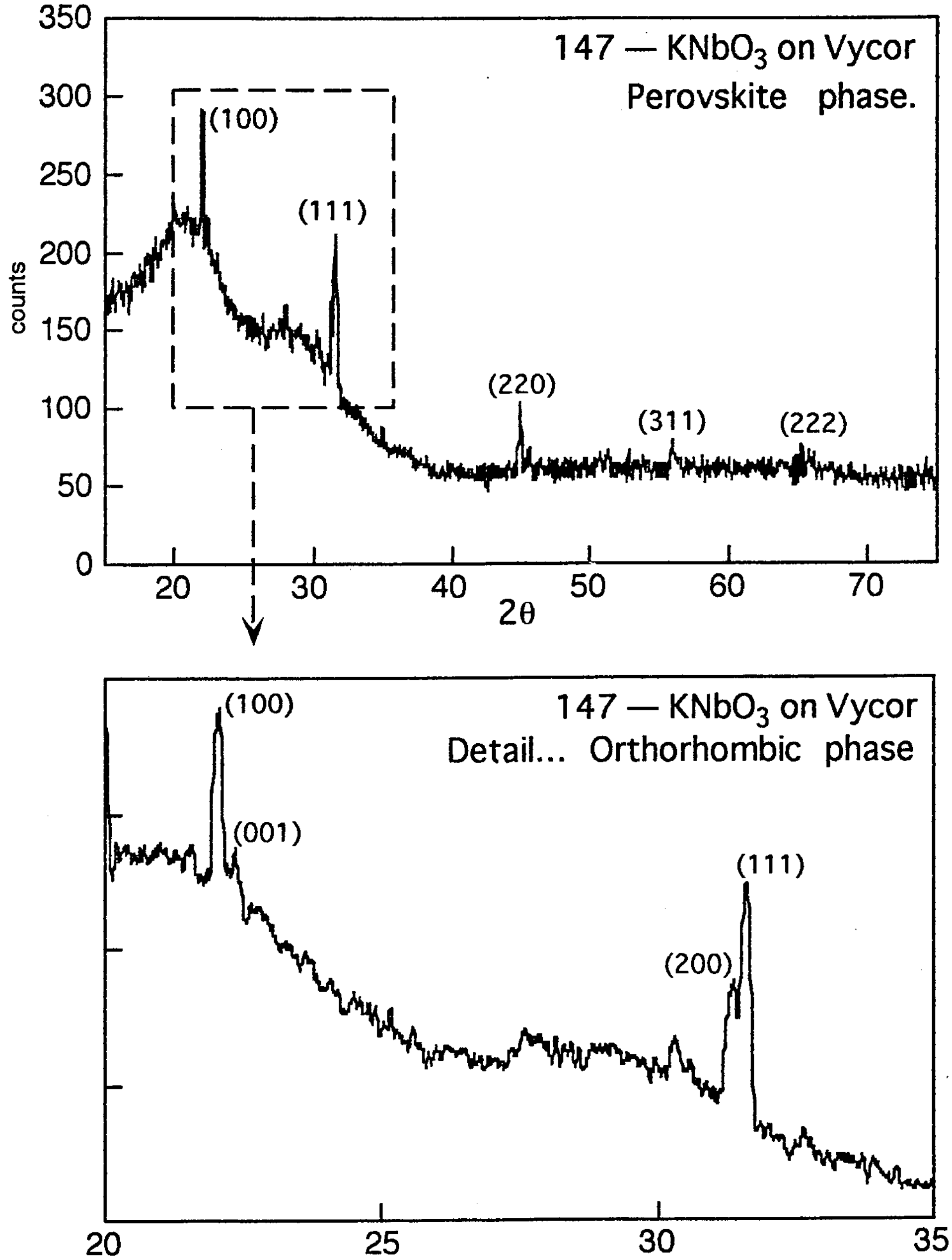
APPENDIX I

Figures



— XRD Scans of $KNbO_3$ on (a) Vycor, (b) Sapphire (0001), and (c) MgO (100)

Figure 1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250
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150
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50
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counts
20
30
40
50
60
70
2θ
147 — KNbO3 on Vycor
Perovskite phase.
(100)
(111)
(220)
(311)
(222)
147 — KNbO3 on Vycor
Detail... Orthorhombic phase
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(001)
(111)
(200)
20
25
30
35

Figure 2

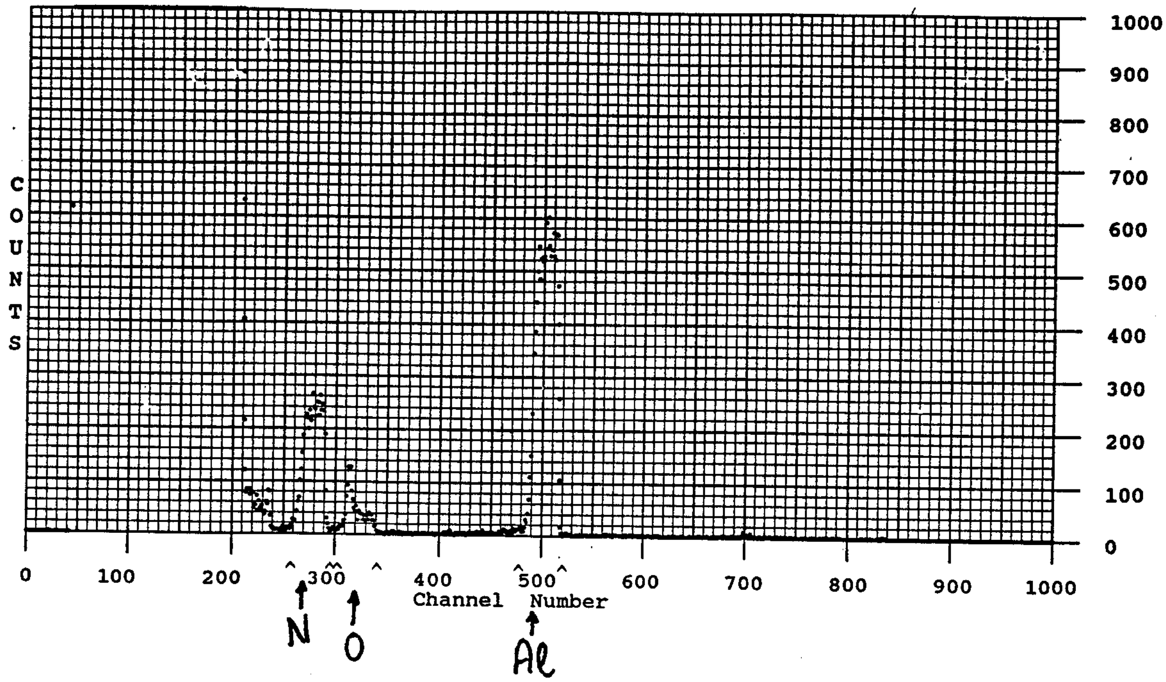
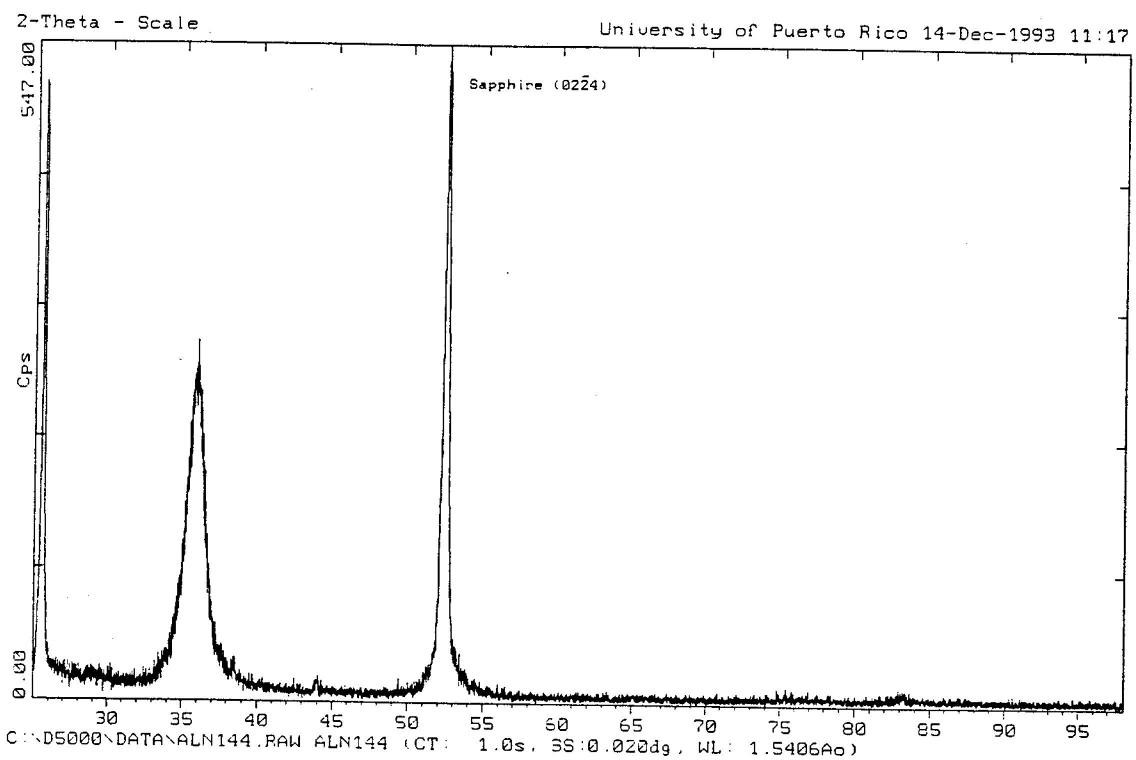


Figure 3. RBS spectrum of AlN sample



XRD scan of AlN film grown on Sapphire substrate

Figure 4